# IN-SITU CLAM EXPOSURE IN THE RAINY RIVER TO DETERMINE THE SOURCE OF ORGANOCHLORINE CONTAMINANTS

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# IN-SITU CLAM EXPOSURE IN THE RAINY RIVER TO DETERMINE THE SOURCES OF ORGANOCHLORINE CONTAMINANTS

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## EXECUTIVE SUMMARY

In 1986, an in-depth study was conducted to evaluate the water quality in the Rainy River, focusing on the impacts of the two Boise Cascade Pulp and Paper mills at Fort Frances and International Falls. The investigation reported herein represents one component of the in-depth study. This investigation was designed to locate the source or sources and determine the spatial distribution of biologically available dioxins, furans and other organochlorine contaminants in the Rainy River by exposing uncontaminated clams at selected locations in the Rainy River and its tributaries and examining the levels of contaminants accumulated in their tissue.

Several organochlorine compounds including PCBs, hexachloroethane, hexachlorobutadiene, DDE, DDT, octachlorostyrene, and chlorinated dioxins, including 2,3,7,8-tetra-chloro-dibenzo-p-dioxins (TCDD) were found in clam tissues.

Hexachloroethane and DDE were not associated with discharges from either mill or any other point sources and the levels of these compounds in clam tissues were low.

Several sources of PCBs were found, including the Fort Frances mill, the International Falls STP and an unidentified source in the vicinity of the International Falls mill. The levels in clam tissues were low (maximum level 126 ng/g in caged clams) and unlikely to have an effect on biota, except in localized areas, based on a "no-effect level" of 110 ng/g (Newell et al. 1987).

Low levels of hexachlorobutadiene were found in clams exposed in the vicinity of both mills both upstream and downstream of the diffuser discharges. This suggests that there are other discharges from one or both mills upstream of the diffuser or there is another source (eg. hydraulic fluids from the dam).

DDT was found in clams below the International Falls mill diffuser only.

Both mills were identified as sources of octachlorostyrene. However, the reason for its presence is not clear since it is not usually found in pulp and paper mill effluent. The levels found in clam tissue were low (maximum level 8.7 ng/g in native clams and 5.0 ng/g in caged clams) and unlikely to have an effect on biota based on a "no-effect level" of 20 ng/g (Newell et al. 1987).

Dioxins, including 2,3,7,8-TCDD, originating from the mills were found in clam tissue 60 km downstream of the mills at or above the "no-effect level" of 3 pg/g (Newell et al. 1987). The highest level of 2,3,7,8-TCDD was 10 pg/g in native clams, which was 2.4 times the level found in caged clams at the same site. The difference probably reflects the long period required for this compound to achieve steady-state equilibrium in clam tissue.

Frog Creek, which discharges into Stanjikoming Bay of Rainy Lake was also identified as a source of 2,3,7,8-TCDD, hepta-chloro-dibenzo-p-dioxin (H7CDD) and octa-chloro-dibenzo-p-dioxins (OCDD). There are three Boise Cascade waste disposal sites on the creek, two of which are closed and one which receives wood waste and sludge from the Fort Frances mill. Since the dioxin congener distribution pattern is similar to that found below the Boise Cascade mills, one or more of the disposal sites is the likely source.

The International Falls mill, International Falls STP, Frog Creek and Big Fork River were identified as sources of the higher chlorinated dioxins, but no biological significance could be placed on the levels of these substances found in clam tissues.

## 1.0 INTRODUCTION

In 1986, an in-depth study was conducted to evaluate the water quality in the Rainy River. The major dischargers to the river are two Boise Cascade pulp and paper mills at Fort Francis, Ontario and International Falls, Minnesota, and five municipal wastewater treatment plants.

Recent studies by the United States Environmental Protection Agency and the Ontario Ministry of the Environment have found 2,3,7,8 TCDD in fish collected from the Rainy River between Fort Francis and the Lake of the Woods. Recent studies on the Niagara River have demonstrated that clams are capable of bioaccumulating dioxins and furans (Ministry of the Environment, unpublished data) as well as other organochlorine compounds (Kauss and Hamdy 1985) during a 3-week exposure period.

The primary objective of this investigation, which represents one component of the in-depth Rainy River study, was to locate the source or sources and deternine the spatial distribution of bioavailable chlorinated dioxins, furans and other organochlorine contaminants by exposing uncontaminated clams at selected locations in the Rainy River and its tributaries.

## 2.0 METHODOLOGY

Clams (*Elliptio complanata*) with a maximum shell length between 65 and 72 mm were collected from Balsam Lake (Victoria County) on July 31, 1986, and maintained in Balsam Lake water with aeration at room temperature in 22 L buckets lined with food-grade plastic inserts. Concentrations of organochlorine contaminants in these clams are usually below the analytical detection limits (Kauss and Hamdy 1985). DDE, on occasion, has been found just above the detection limit of 1 ng/g.

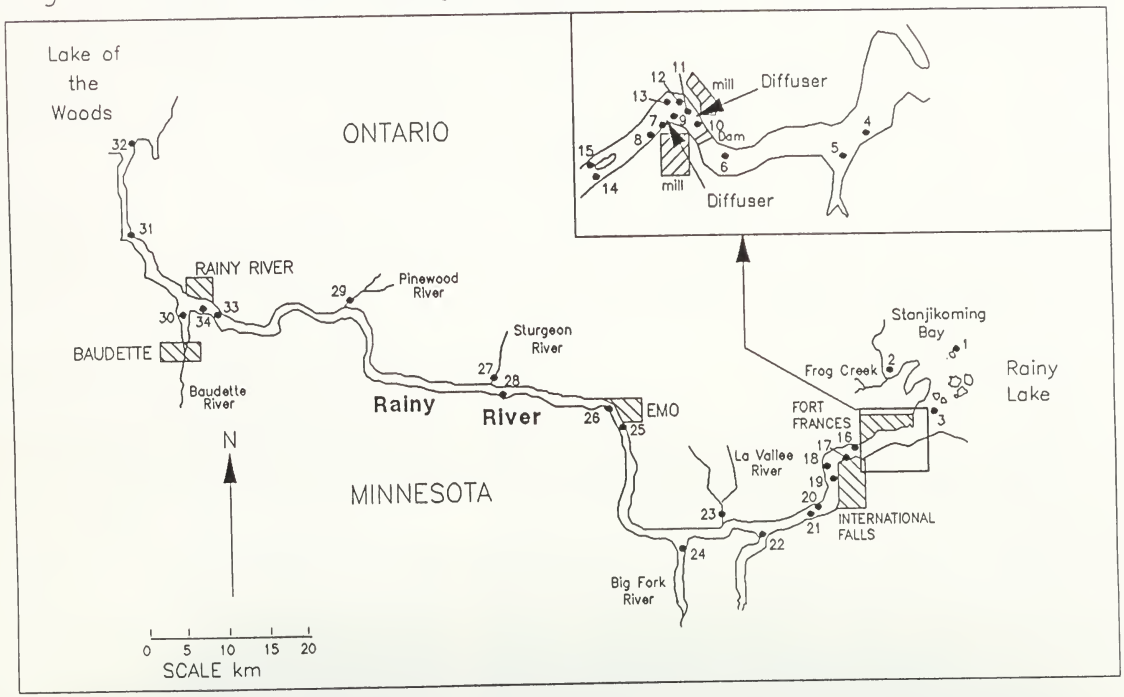
On August 5-7, 1986, clams were placed in envelope-shaped cages 30 cm by 45 cm constructed of 1.25 cm galvanized mesh poultry netting. At each of the 34 stations shown in Figure 1, 3 cages containing 5 clams each were placed on the substrate.

On August 25-27, 1986, after an exposure period of 21±1 days, the caged clams were collected. At stations 4, 18, 28 and 31 (Figure 1), native clams were collected by SCUBA diver. The clams were immediately shucked, wrapped individually in hexane-rinsed foil, frozen on dry ice and shipped to the Ministry of the Environment (OMOE) Laboratory in Rexdale, Ontario. Clam tissue was stored at -20 degrees C prior to analysis.

All analyses were conducted using the analytical methods described in the Ontario Ministry of the Environment "Handbook of Analytical Methods for Environmental Samples"(OMOE 1983). The soft tissues of individual clams were used for all analyses, except chlorinated dioxins and furans where 3 clams were composited for one analysis. Furan analyses have not been completed due to analytical problems and will be reported under separate cover once these problems have been resolved.

In some cases, 3 replicate analyses were performed which permitted statistical analysis of the data. In such cases, the data were statistically analyzed using a one-way ANOVA. If the one-way ANOVA indicated a significant difference among stations ($P<0.05$), then a Tukey's Honestly Significant Difference (HSD) Test (Steel and Torrie 1960) was performed to identify homogeneous groups ($P<0.05$).

Fig. 1. STUDY AREA and cage locations (1–34).



## 3.0 RESULTS

For the presentation of the results, the stations have been separated into five groups as follows:

1. Control stations, consisting of five stations located upstream of the influence of the mills (stations 1, 2, 3, 4, 5, 6);

2. Fort Frances stations, within the influence of the Fort Frances mill, consisting of stations on the Canadian side of the Rainy River, ranging from immediately upstream of the Fort Frances mill diffuser downstream to station 18, which was 4.5 km below the mill (stations 10, 11, 12, 13, 15, 18);

3. International Fall stations, within the influence of the International Falls mill, consisting of stations on the American side of the Rainy River, ranging from immediately upstream of the International Falls mill diffuser downstream to station 19, which was 4.5 km below the mill (stations 7, 8, 9, 14, 17, 19);

4. All stations in the Rainy River and Lake of the Woods, downstream of the above three groups, where complete horizontal and vertical mixing of the effluent had taken place (stations 20, 21 25, 26, 28, 31, 32, 33, 34);

5. Big Fork River station (station 24).

### 3.1 PCBs

#### Statistical Analysis

At 8 of the stations, which consisted of four of the control stations, two within the influence of the Fort Frances mill, and two >60 km below the mills and therefore potentially influenced by both mills, three replicate samples were analyzed which permitted a statistical analysis of the data. The one-way ANOVA indicated a significant difference among the stations ($P<0.0002$). Tukey's HSD test indicated that the stations belonged to 3 homogeneous groups (Table 1).

Table 1: Division of stations into homogeneous groups based on Tukey's HSD Test for PCBs in Clams

| Station # | Location Description | Conc. (ng/g) | Group |
|---|---|---|---|
| 1 - 4 | Controls | <20 | 1 |
| 32 | Lake of the Woods | 30 | 1 2 |
| 10 | Fort Francis mill diffuser | 60 | 2 |
| 28 | Sturgeon R. 60 km downstream | 79 | 2 3 |
| 18 | 4.5 km downstream of mill Canadian side | 118 | 3 |

Spatial Distribution

At the control stations, PCBs in both caged and native clams were less than the detection limit of 20 ng/g (Table 2, Figure 2).

At the Fort Frances stations, PCBs were below the detection limit above the mill diffusers. Between the mill diffusers and 4.5 km downstream, the levels of PCBs varied between 47 and 118 ng/g. At station 18, 4.5 km downstream of the mill, the levels of PCBs were significantly higher ($P<0.05$) than directly below the mill diffuser at station 10. At station 18 the levels of PCBs in the native clams (Lampsilis radiata) were 148 ng/g.

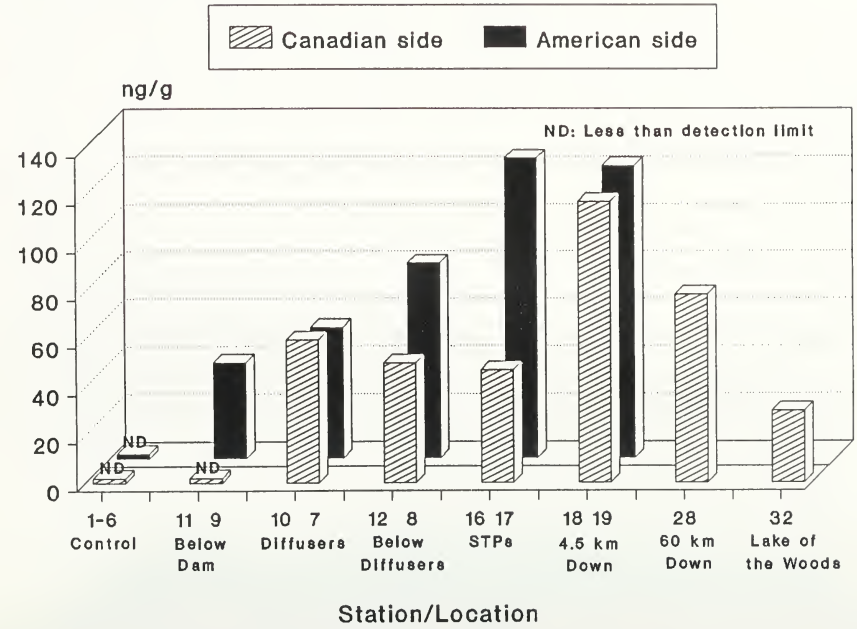
At the International Falls stations, PCBs were above the detection limit in caged clams both upstream and downstream of the diffusers. Although a statistical evaluation could not be made because replications were not conducted, it appeared that the levels found in caged clams were higher downstream at both station 17, below the

Table 2: Concentration of Organochlorine Contaminants in Clams Exposed in the Rainy River (ng/g wet weight (Standard Deviation))

(ND = Less than detection limit)

| STATION | LOCATION DESCRIPTION | # REPS | Hexa-chloro-ethane | Hexa-chloro-butadiene | PCB total | PP-DDE | PP-DDT | Octa-chloro-styrene |
|---|---|---|---|---|---|---|---|---|
| 1 | RAINY LAKE - Prospect Bay | 3 | ND | ND | ND | 2.3 (3.2) | ND | ND |
| 2 | FROG CREEK - Mouth | 3 | ND | ND | ND | ND | ND | ND |
| 3 | PITHERS POINT - Introduced clams | 3 | ND | ND | ND | 3.2 (2.4) | ND | ND |
| 4 | PITHERS POINT - Native clams | 3 | ND | ND | ND | ND | ND | ND |
| 5 | MOONLIGHT ROCK CREEK | 1 | ND | ND | ND | 6.0 | ND | ND |
| 6 | ABOVE DAM | 1 | ND | ND | ND | ND | ND | ND |
| 7 | INTERNATIONAL FALLS - Diffuser | 3 | ND | 5.2 (4.1) | 54.7 (14.6) | ND | ND | 3.0 |
| 8 | INTERNATIONAL FALLS - Below Diffuser | 1 | ND | 4.0 | 82.0 | ND | 57.0 | 4.0 |
| 9 | INTERNATIONAL FALLS - Control | 1 | ND | 7.0 | 40.0 | ND | ND | ND |
| 10 | FORT FRANCIS - Diffuser | 3 | ND | 7.3 (2.9) | 60.3 (16.1) | 1.0 (0.9) | ND | 2.7 (0.6) |
| 11 | FORT FRANCIS - Control | 1 | ND | 10.0 | ND | ND | ND | ND |
| 12 | FORT FRANCIS - Below Diffuser | 1 | ND | 7.0 | 50.0 | ND | ND | 3.0 |
| 16 | FORT FRANCIS - STP | 1 | ND | ND | 47.0 | ND | ND | 2.0 |
| 17 | INTERNATIONAL FALLS - STP | 1 | ND | ND | 126.0 | ND | ND | 5.0 |
| 18 | 4.5km BELOW MILL CANADIAN SIDE -Introduced clams | 3 | 1.5 (0.9) | ND | 118.3 (14.6) | ND | ND | 2.7 (0.6) |
| 18 | 4.5km BELOW MILL CANADIAN SIDE -Native clams | 3 | ND | ND | 148.3 (38.6) | 3.3 (1.2) | ND | 8.7 (2.1) |
| 19 | 4.5km BELOW MILL AMERICAN SIDE | 1 | ND | ND | 123.0 | ND | ND | 4.0 |
| 24 | BIG FORK RIVER - Upstream of mouth | 1 | ND | ND | ND | ND | ND | ND |
| 28 | STURGEON RIVER - Introduced clams | 3 | ND | ND | 78.7 (34.0) | ND | ND | 1.5 (0.9) |
| 28 | STURGEON RIVER - Native clams | 3 | ND | ND | 56.7 (14.3) | ND | ND | 1.0 (0.9) |
| 32 | LAKE OF THE WOODS - Introduced clams | 3 | ND | ND | 30.3 (3.1) | ND | ND | ND |
| 32 | LAKE OF THE WOODS - Native clams | 3 | ND | 1.0 (1.9) | 90.7 (70.5) | ND | ND | ND |

# Figure 2: Concentration of PCBs in Clams Exposed in the Rainy River



International Falls STP (126 ng/g) and 4.5 km downstream of the mill at station 19 where levels of PCBs were 123 ng/g (Table 2, Figure 2).

Sixty km downstream of the mills at station 28, where complete horizontal and vertical mixing had taken place, the levels in caged clams were not significantly different ($P<0.05$) from the levels found below the Fort Frances mill (station 10). The levels were 79 ng/g in introduced clams and 57 ng/g in the native clams Lampsilis radiata. In the Lake of the Woods, the mean levels were 30 ng/g in caged clams, which was not significantly different ($P<0.05$) from levels found immediately below the mill or 60 km below the mill (station 10). The levels were, however, significantly lower than those at station 18, 4.5 km below the Fort Frances mill. The levels were 91 ng/g in the native clam Anodonta sp. in the Lake of the Woods (station 32). This was the only station where Anodonta sp. were analyzed and the only station where the levels in native clams were markedly different from caged clams.

### 3.2 Organochlorine Pesticides and Chlorinated Benzenes

Several contaminants, including hexachloroethane (HCE), hexachlorobutadiene (HCBD), pp-DDE, pp-DDT and octachlorostyrene (OCS) were found in clam tissues (Table 2).

#### Hexachloroethane

HCE was found in caged clams at station 18, 4.5 km below the mill on the Canadian side of the river but was below the detection limit of 1 ng/g at all other stations (Table 2).

#### Hexachlorobutadiene

HCBD was below the detection limit (1 ng/g) in clams exposed upstream of the mills.

At the Fort Frances stations, HCBD was found at 10 ng/g at station 10 located downstream of the dam but upstream of the mill diffuser. Below the mill diffuser, the levels were 7 ng/g at both station 10 and 12. At the other Fort Frances stations, HCBD was less than the detection limit (Figure 3, Table 2).

At the International Falls stations, HCBD levels in clams followed a similar pattern to that found at the Fort Frances mill. Directly upstream of the diffusers, the maximum levels of HCBD were found (7 ng/g) and detectable levels were found in clams for a short distance downstream of the mill (Figure 3, Table 2).

HCBD was below the detection limit in clams from all other stations except in native clams (Anodonta sp.) from Lake of the Woods where levels were 1 ng/g.

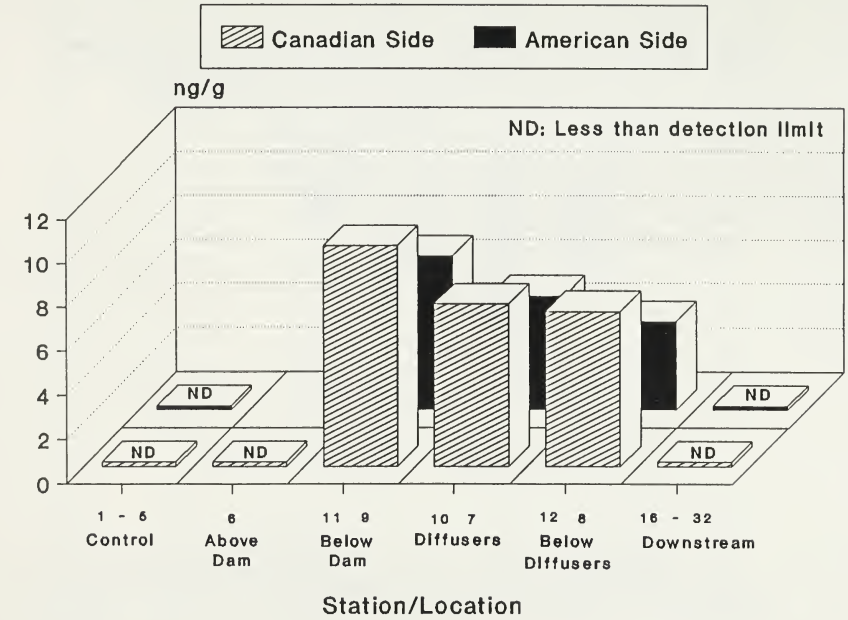
DDE and DDT

In Rainy Lake and in the Rainy River upstream of the mills, the levels of pp-DDE ranged from below the detection limit (1 ng/g) to 6.0 ng/g (Table 2). Below the mills, pp-DDE was non-detectable except at two stations, the Fort Frances diffuser (1 ng/g) and 4.5 km below the mill on the Canadian side of the river (3.3 ng/g). DDT was found only at one station, International Falls below the mill diffuser where the level was 57 ng/g.

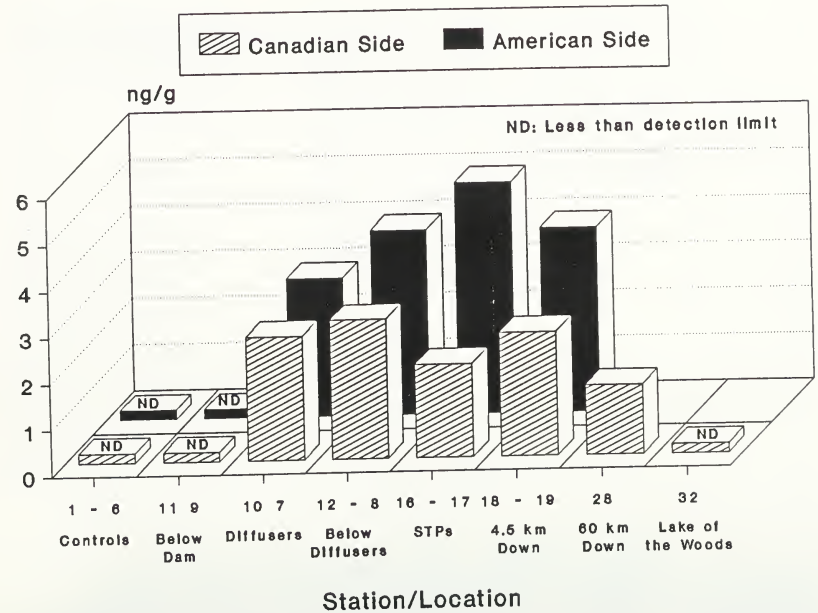
Octachlorostyrene

OCS was non-detectable upstream of the mills. At the Fort Frances stations, detectable levels (2.7-3.0 ng/g) were found in caged clams below the mill diffusers (Table 2, Figure 4). Downstream, 4.5 km below the mill at station 18, the level of OCS in caged clams was 2.7 ng/g. OCS in native clams from the latter station were the highest recorded in the study at 8.7 ng/g.

# Figure 3: Concentration of HCBD in Clams Exposed in the Rainy River



# Figure 4: Concentration of OCS in Clams Exposed in the Rainy River



At the International Falls stations, detectable levels of OCS (3-5 ng/g) were found in clams at all stations below the mill diffuser.

Sixty km below the mills at station 28, the levels of OCS were 1.5 ng/g. Further downstream and in the Big Fork River, the levels were below the detection limit of 1 ng/g.

3.3 Chlorinated Phenols

Chlorinated phenols were to have been analyzed in clams from the same stations as the PCBs and pesticides. However, a freezer malfunction precluded these analyses. The loss of these data cannot be considered critical because recent studies (Metcalfe and Hayton 1988) have demonstrated that clams do not bioaccumulate chlorinated phenolic compounds. The bait leech, Nephelopsis obscura is a more appropriate organism for assessing the biological availability of chlorinated phenolic compounds. A study using this organism to evaluate chlorinated phenols in the Rainy River was conducted concurrently by Metcalfe (1988).

3.4 Chlorinated Dioxins

Clams from two stations upstream of the mills were analyzed for dioxins. At the mouth of Frog Creek (station 2) which flows into Stanjikoming Bay of Rainy Lake, clams exposed for the 3-week period had 4.7 pg/g of 2,3,7,8-TCDD, 20 pg/g of H7CDD and 6.9 pg/g of OCDD (Table 3, Figures 5 and 6).

At Pithers point (station 4) which is upstream of the mills in the Rainy River, dioxins in clams were below the level of detection for all congeners (Table 3, Figures 5 and 6).

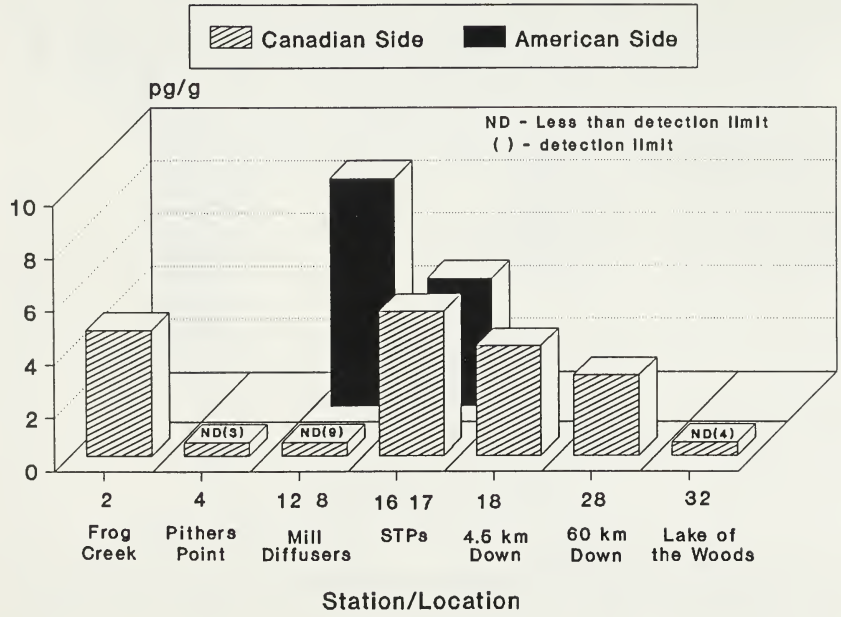
Immediately downstream of the Fort Frances mill diffusers (station 12), all congeners of dioxins were below the detection limit

Table 3: Concentration of Chlorinated Dioxins in Clams in the Rainy River in pg/g wet weight

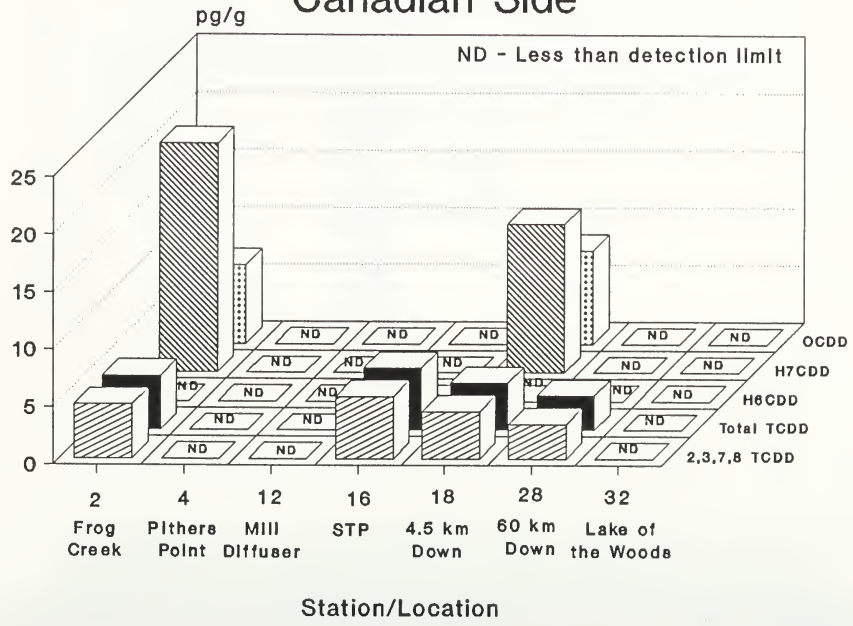
| Station Number | Location | 2378-TCDD | Total TCDD | P5CDD | H6CDD | H7CDD | OCDD |
|---|---|---|---|---|---|---|---|
| 2 | Frog Creek | 4.7 | 4.7<1> | ND(0.8) | ND(4) | 20<1> | 6.9 |
| 4 | Pithers Point | ND(3) | ND(3) | ND(2) | ND(2) | ND(5) | ND(10) |
| 8 | International Falls below diffuser | 8.6 | 13<2> | ND(1) | 3.4<1> | 15<1> | 4.8 |
| 12 | Fort Frances below diffusers | ND(9) | ND(9) | ND(6) | ND(20) | ND(40) | ND(20) |
| 16 | Fort Frances STP | 5.4 | 5.4<1> | ND(5) | ND(1) | ND(10) | ND(10) |
| 17 | International Falls STP | 4.8 | 4.8<1> | ND(4) | ND(20) | ND(20) | 58 |
| 18 | 4.5 km down Canadian side | 4.1 | 4.1<1> | ND(3) | ND(6) | 13<1> | 8.2 |
| 18 | 4.5 km down Canadian side Native clams | 10 | 10<1> | ND(2) | ND(4) | 11<2> | 6.9 |
| 24 | Big Fork River | ND(1) | ND(1) | ND(10) | ND(1) | 6.3<1> | 8.6 |
| 28 | 60 km down Canadian side | 3.0 | 3.0<1> | ND(2) | ND(8) | ND(10) | ND(8) |
| 32 | Lake of the Woods | ND(4) | ND(4) | ND(5) | ND(10) | ND(30) | ND(20) |

ND( ) - Less than the detection limit shown in brackets
< > - number of isomers detected

# Figure 5: Concentration of 2,3,7,8 TCDD in Clams exposed in the Rainy River



# Figure 6: Concentration of Dioxins in Clams exposed in the Rainy River Canadian Side



(Table 3, Figures 5, 6). However, the analytical recovery rates were low which resulted in high detection limits for this sample. For 2,3,7,8-TCDD, the detection limit was 9 pg/g. Further downstream, at the Fort Frances STP (station 16), 2,3,7,8-TCDD was found in clams at 5.4 pg/g. All other dioxin congeners were below the detection limits. At station 18, 4.5 km below the Fort Frances mill, 2,3,7,8-TCDD was found in clams at 4.1 pg/g. H7CDD and OCDD were found at 13 pg/g and 8.2 pg/g respectively. Native clams from this site had levels of 2,3,7,8-TCDD of 10 pg/g. H7CDD and OCDD levels were 11 pg/g and 6.8 pg/g respectively.

Immediately downstream of the International Falls mill diffuser (station 8), 2,3,7,8-TCDD was found in caged clams at 8.6 pg/g, and total TCDD was 13 pg/g (Table 3, Figure 5). H6CDD, H7CDD, and OCDD were found at 3.4 pg/g, 15 pg/g and 4.8 pg/g respectively. Further downstream below the International Falls STP (station 17), 2,3,7,8-TCDD was present at 4.8 pg/g. H6CDD and H7CDD were below detection limits but detection limits were high. OCDD was present at 58 pg/g.

Clams exposed in the Big Fork River (station 24) had 6.3 pg/g of H7CDD and 8.6 pg/g of OCDD. Other dioxin congeners were below the detection limits.

Sixty km downstream of the mills at station 28, 2,3,7,8-TCDD was present at 3.0 pg/g. All other dioxin congeners were below the detection limits. Clams exposed in the Lake of the Woods were below the detection limits for all congeners.

## 4.0 DISCUSSION

### 4.1 PCBs

Since all clams analyzed from stations upstream of the mills were below the detection limit, there do not appear to be any major

sources of PCBs in the Rainy River system upstream of the Boise Cascade Mills.

The Fort Frances mill was identified as a source of PCBs because the mean concentration of PCBs in clam tissues was 60 ng/g directly below the diffuser compared to concentrations which were below detection at all stations upstream of the diffuser. No other point sources of PCBs were identified on the Canadian side of the river. However, significantly higher levels ($P<0.05$) of PCBs (123 ng/g) were found 4.5 km below the mill relative to the levels found at the Fort Frances mill diffuser, suggesting that there were additional inputs of PCBs from the Canadian side of the river. An alternate hypothesis is that effluent from the American side of the river was contributing to the higher levels at this station; however, dispersion studies conducted by Beak suggest that this was unlikely.

At the International Falls stations, PCBs were found upstream and downstream of the mill diffuser at similar levels. Since sufficient replications were not conducted to statistically analyze the data, the mill diffuser could not be confirmed as a source of PCBs. However, the data do suggest that there was an active source of PCBs in the vicinity of the International Falls mill. In addition to a source in the vicinity of the mill, high levels of PCBs in caged clams downstream of the International Falls STP and 4.5 km below the mill suggest that the STP was a source.

Levels of PCBs in clams remained above the detection limit down the Rainy River and into the Lake of the Woods indicating that, either there were additional sources of PCBs in the lower river, or that the PCBs from Fort Frances and International Falls were biologically available for the entire reach of the river. The sampling design did not provide adequate resolution to identify if

there were additional sources. In other studies (Ministry of the Environment, unpublished data), the level of PCBs accumulated by clams tends to decline rapidly with distance from the source, probably because the PCBs become bound to particulate matter and are deposited in quiescent areas. In the Rainy River, however, there appeared to be few depositional areas where PCB contaminated suspended sediments could be deposited, which may have contributed to the biological availability of PCBs over a greater distance than expected. To strengthen the hypothesis that there are no other major sources of PCBs between the stations 4.5 km below the mills and Lake of the Woods, the spatial pattern of PCBs in clam tissue was compared to that of 2,3,7,8-TCDD and octachlorostyrene, for which there are likely no other sources below the mills. The spatial distribution of bioavailability of these compounds was similar to PCBs, that is, only a gradual decline was observed in the levels found in clams between the mills and Lake of the Woods.

PCBs have not been found to be a problem in sportfish taken from the Rainy River or Lake of the Woods (Ministry of the Environment 1988). The levels in sportfish have remained well below the human consumption guideline of 2000 ng/g established by Health and Welfare Canada and in many cases have been below the guideline of 110 ng/g, which is considered to be adequate to protect the most sensitive fish-eating birds and mammals (Newell et al. 1987). Similarly, in this study, the levels in clams were low, and, except in localized areas, were below the level considered to be the "no-effect" level. The "no-effect" level of 110 ng/g, as mentioned previously, was developed to protect wildlife from the consumption of hazardously contaminated forage fish. The no-effect levels established by Newell et al. (1987) were based on laboratory feeding studies using native wildlife or surrogate domestic animals. A safety factor was applied to the lowest observed effect level to establish the "no-effect level". Since clams represent

a food source for some of the wildlife considered by Newell et al. (1987), we feel that a similar level for clam tissue is appropriate to protect wildlife. In our interpretation of the levels established by Newell et al. (1987), we assume that there will be no adverse effects on piscivorous wildlife if the levels found in clams are below the "no-effect level". If the levels in clams are above the "no-effect level" then there is the potential for adverse impacts to occur.

## 4.2 Organochlorine Pesticides and Chlorinated Benzenes

### Octachlorostyrene

Although OCS is generally not found in pulp and paper mill effluents, the data from this study indicate that it is being discharged from both mills. The levels in clams were well below the "no-effect" level of 20 ng/g established to protect fish-eating birds and mammals (Newell et al. 1987), reaching a maximum of 8.7 ng/g at 4.5 km below the Canadian mill. Detectable levels did persist as far downstream as 60 km below the mills.

Both laboratory and field studies of the St. Clair River have demonstrated that the exposure time for clams to reach equilibrium for OCS exceeds the 3-week exposure used in this study (Muncaster et al. 1987). In the present study, a comparison was made between native clams and clams exposed for a 3-week period. The native clams had significantly higher levels of OCS than those exposed for 3 weeks ($P<0.009$) by a factor of about three. Assuming a similar ratio of OCS between native clams and introduced clams for all locations, the maximum levels of OCS in native clams (if they had been present) would have been approximately 15 ng/g below the International Falls STP, which is still below the no-effect level.

Hexachlorobutadiene

The distribution of HCBD in clams indicated that the source or sources of HCBD were below the station located upstream of the dam and above the mill diffusers. The levels were low, with a maximum of 10 ng/g, and were detectable for only a short distance downstream of the mills, except for low levels found in native clams in the Lake of the Woods. The "no-effect" level for this compound is 1300 ng/g (Newell et al. 1987).

Although the data suggest that the source of the HCBD is not the mill diffusers, effluent monitoring of the Fort Frances mill by the Ministry of the Environment in February 1986 revealed that HCBD was present in the mill effluent at 11 ng/L. This suggests that: 1) one or both mills were at least intermittent sources and that there are other discharges from one or both mills upstream of the diffusers; or 2) alternatively, that there is another source (e.g. hydraulic fluids from the dam).

DDT and Metabolites

The low levels of pp-DDE found in clams from 5 stations reflect the previous wide-spread use of the parent compound, DDT. No point sources were identified. DDT, on the other hand, was found only in clams from below the International Falls diffuser and, in addition, was found in mill effluent during the clam exposure period (Flood et al. 1989), indicating that the mill was the source. The level of 57 ng/g found in clams is well below the accepted "no-effect" level of 200 ng/g for the total of DDT and its metabolites (Newell et al. 1987).

4.3 Dioxins

The purpose of the dioxin study was to determine the sources and spatial extent of biologically availabile dioxins in the Rainy River watershed. The purpose was not to determine the biological

significance of the levels found in clams in this study.

The biological availability of dioxin congeners appears to be related to the degree of chlorination (MOE 1985). Studies conducted primarily on fish indicate that the lower chlorinated dioxins such as TCDDs are more bioaccumulative and persistent than the higher chlorinated dioxins such as the OCDDs. Studies conducted by the Ministry of the Environment on the Niagara River suggest a similar pattern of uptake for clams (MOE unpublished data).

The levels of 2,3,7,8-TCDD as well as H7CDD and OCDD found in caged clams at station 2 indicate that there is a source of these compounds in the Frog Creek watershed. There are three disposal sites on the creek, one of which is currently active and receives wood waste and sludge from the mill. The dioxin congener distribution pattern found in clams is similar to that found below the Biose Cascade mills on the Rainy River which suggests that one or more of the disposal sites is the source. Further work is currently being undertaken to identify the specific source or sources and the mode of entry of the dioxins to the creek.

At the Fort Frances stations, dioxins were first detected below the Fort Frances STP where 2,3,7,8-TCDD was found at 5.4 pg/g. However, it is suspected that the source was the Fort Frances mill rather than the STP and that the non-detectable levels in clams at the mill diffuser were the result of the high detection levels (9 pg/g for 2,3,7,8-TCDD) in this sample.

Downstream, 4.5 km below the Fort Frances mill, the levels of 2,3,7,8-TCDD were not substantially lower than the levels found in clams just downstream of the Fort Frances mill. This was not unexpected because dispersion studies conducted by Beak Consultants

Limited in 1986 indicated little dilution of the mill effluent close to shore between 1 km and 4.5 km below the mill. However, it was unexpected that H7CDD and OCDD not found at the Fort Frances STP station would have been found here. Dispersion studies indicate that there would have been little horizontal mixing between the American and Canadian sides of the river making it unlikely that the additional dioxin congeners originated from the American side of the river.

The International Falls mill diffuser was identified as a source of 2,3,7,8-TCDD, one other isomer of TCDD, H6CDD, H7CDD and OCDD. It was not unexpected to find H7CDD and OCDD since these congeners are often associated with chlorinated phenols (MOE 1985), nor was it unexpected to find 2,3,7,8-TCDD since this isomer has been found in sludge from the mill. Downstream, below the International Falls STP, 2,3,7,8-TCDD levels found in clams were lower than those found below the mill suggesting that there were no additional inputs from the STP. However, the high levels of OCDD appeared to come from the STP, since the levels found here were approximately an order of magnitude higher than below the mill diffuser (58 pg/g versus 4.8 pg/g) and because municipal STPs are often sources of this isomer (MOE 1985).

The Big Fork River had been identified as a potential source of 2,3,7,8-TCDD based on the industries present on the river. Only the less toxic and more ubiquitous H7CDD and OCDD were found in the clams. Since the detection limits for analysis were low enough, (1 pg/g for 2,3,7,8-TCDD) the Big Fork River is not a source of 2,3,7,8 TCDD.

Sixty km below the mills, detectable levels of 2,3,7,8-TCDD (3.0 pg/g) were found in clams. This reflects the findings for other contaminants (e.g. PCBs, OCS) which appear to be biologically

available for a long distance downstream of the sources for reasons outlined previously in the discussion of PCBs.

Clams exposed in the Lake of the Woods (near the mouth of the Rainy River) were below the detection limit for all dioxin congeners, indicating that residual effects from sources at Fort Frances and International Falls were not evident and that there were no additional sources.

To determine if the levels of dioxins were approaching equilibrium in the clams exposed for 3 weeks, native clams from the station 4.5 km below the mill were analyzed and compared to clams exposed at the same location for 3 weeks. The level of 2,3,7,8-TCDD found in native clams was about 2.4 times that of the introduced clams (10 pg/g versus 4.1 pg/g) indicating that a substantially longer period than 3 weeks is required to achieve equilibrium. The levels of the higher chlorinated H7CDD and OCDD were similar in both native and introduced clams suggesting that the introduced clams had achieved equilibrium. Considering that 2,3,7,8-TCDD is known to be highly bioaccumulative and persistent and the higher chlorinated dioxins tend to be much less bioaccumulative (OMOE 1985), our findings were consistent with those of other studies (OMOE 1985).

Little information is available on either the uptake of 2,3,7,8-TCDD by clams or the biological significance of levels found in clams. Newell *et al.* (1987) established a "no-effect level" of 3 pg/g 2,3,7,8-TCDD in forage fish to protect the most sensitive fish-eating mammals and birds. Since clams also represent a food source for birds and mammals, it can be argued that a similar level (3 pg/g) for clam tissue is appropriate. The levels of 2,3,7,8-TCDD in tissue from caged clams equalled or exceeded this level for a distance of at least 60 km down the Rainy River, suggesting the possibility of biological impacts for over 60 km of river.

There was evidence that the caged clams had not achieved a steady-state equilibrium with environmental levels of 2,3,7,8-TCDD. Native clams at one station were 2.4 times higher than caged clams. Using this factor at all locations, the maximum predicted level in native clams would have been approximately 21 pg/g directly below the International Falls mill, gradually declining to approximately 7 pg/g 60 km below the mills. Again applying the 3 pg/g criterion as the "no-effect level", both the possibility and the extent of the impacts increases.

## 5.0 CONCLUSIONS

1. Several sources of PCBs were found, including the Fort Frances mill, the International Falls STP, and an unidentified source in the vicinity of the International Falls mill.

2. Both the Fort Frances and International Falls mills were identified as sources of octachlorostyrene. No explanation could be given for its presence, since it is generally not found in pulp and paper mill effluents.

3. Hexachlorobutadiene was found near both mills but did not appear to be associated solely with the diffuser discharges.

4. The International Falls mill was identified as a source of DDT.

5. Both mills were identified as sources of 2,3,7,8-TCDD, and measurable levels of bioavailable 2,3,7,8-TCDD in clams were found 60 km down the Rainy River.

6. Frog Creek was identified as a source of 2,3,7,8-TCDD. The source within the watershed was not identified; however, it is likely that one or more of the Boise Cascade landfill sites near the Creek was the source.

7. Contaminants originating from sources at Fort Frances and International falls were biologically available for >60 km down the Rainy River probably because of the lack of depositional areas in the river.

8. With the exception of dioxins, it is unlikely that the levels of organochlorine contaminants found in clams would have had a significant impact on biota since the levels were generally below the "no-effect levels" reported by Newell et al. (1987).

9. Although the assessment of the impact of the levels of 2,3,7,8-TCDD found in clams is highly speculative, the data suggest that there is the potential for biological impacts for at least 60 km of the Rainy River. When the levels found in clams are "corrected" to steady-state equilibrium levels, the distance over which biological impacts could occur increases.

10. The Big Fork River was identified as a source of H7CDD and OCDD.

## 6.0 RECOMMENDATIONS

1. Since HCBD and PCBs were found in the vicinity of but upstream of the diffusers of the mills, studies should be undertaken to determine if untreated effluent from one or both mills is entering the river upstream of the diffusers.

2. Studies of the Frog Creek watershed should be undertaken to identify the source(s) of 2,3,7,8-TCDD.

3. Since the levels of 2,3,7,8-TCDD found in clams indicated that biological impacts could be occurring, measures should be taken to reduce or eliminate the discharge of this compound from these mills.

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